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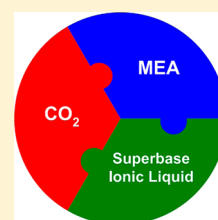
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S Supporting Information

ABSTRACT: The miscibility of monoethanolamine (MEA) in five superbase ionic liquids (ILs), namely the trihexyl-tetradecylphosphonium benzotriazolide ([P₆₆₆₁₄][Bentriz]), trihexyl-tetradecylphosphonium benzimidazolide ([P₆₆₆₁₄][Benzim]), trihexyl-tetradecylphosphonium 1,2,3-triazolide ([P₆₆₆₁₄][123Triz]), trihexyl-tetradecylphosphonium 1,2,4-triazolide ([P₆₆₆₁₄][124Triz]), and trihexyl-tetradecylphosphonium imidazolide ([P₆₆₆₁₄][Im]) was determined at 295.15 K using ¹H NMR spectroscopy. The solubility of carbon dioxide (CO₂) in equimolar (IL + MEA) mixtures was then studied experimentally using a gravimetric technique at 295.15 K and 0.1 MPa. The effect of MEA on the CO₂ capture ability of these ILs was investigated together with the viscosity of these systems in the presence or absence of CO₂ to evaluate their practical application in CO₂ capture processes. The effect of the presence of MEA on the rate of CO₂ uptake was also studied. The study showed that the MEA can enhance CO₂ absorption over the ideal values in the case of [P₆₆₆₁₄][123Triz] and [P₆₆₆₁₄][Bentriz] while in the other systems the mixtures behave ideally. A comparison of the effect of MEA addition with the addition of water to these superbase ILs showed that similar trends were observed in each case for the individual ILs studied.



1. INTRODUCTION

Carbon dioxide is a greenhouse gas that is released into the atmosphere from flue gas streams. It is believed that CO₂ currently contributes to 60% of the greenhouse gases released into the atmosphere.¹ With global CO₂ emissions set to increase there is a real and immediate need to develop a process that can effectively and efficiently capture CO₂ before being released into the atmosphere. The sources of CO₂ include mobile and stationary sources with the latter associated predominantly from power plants in the form of flue gas streams. As well as emissions of CO₂, it is also present in significant concentrations in biogas and natural gas. In these systems, the CO₂ limits the combustion of the methane and must be separated before the gas can be utilized as a fuel. In both emissions and methane containing streams, efficient separation is critical for both economic and environmental reasons. To enable these types of separations, industrial practice is currently dominated by aqueous alkanolamine solvents (e.g., 30 wt % aqueous monoethanolamine (MEA)) where a chemical reaction occurs between the CO₂ and amine solution. This process is attractive due to the low cost of solvent, high reactivity, and an absorption capacity of 1:2 mol of CO₂ per mole of solvent ratio.^{2,3} These advantages are offset by the volatile and corrosive nature of the aqueous solvent mixtures and the high energy consumption needed for regeneration with an enthalpy of regeneration of CO₂,⁴ $\approx 66.7\text{--}76.9\text{ kJ}\cdot\text{mol}^{-1}$, leading to high operational costs and environmental impact.^{5,6} Due to these disadvantages there has been a recent increase in interest in the search for a more suitable solvent for postcombustion CO₂ capture.

In this respect ionic liquids (ILs) have received an increasing amount of interest in recent years as an alternative solvent for CO₂ capture due to their potential as environmentally friendly or "green" solvents. ILs have highly attractive properties such as high thermal stability, negligible vapor pressure, and their ability to be task specific.⁷ Blanchard et al.⁸ were the first to report high CO₂ solubility in imidazolium-based ILs reaching a CO₂ mole fraction of 0.6 at 8 MPa and 298.15 K. It has also been shown that imidazolium ILs containing the bis-[(trifluoromethyl)sulfonyl]imide ([NTf₂])[−] anion have a high affinity for CO₂ capture,⁹ in comparison with hexafluorophosphate-based ILs, for example.¹⁰ However, many of these ILs only absorb the CO₂ physically and, unfortunately, their CO₂ capacity is too low to be industrially viable. However, by adding basic character to the IL it was observed that the CO₂ capacity could be increased. Bates et al.¹¹ synthesized the first IL with an amine moiety, which resulted in an increase of the CO₂ capacity driven by chemical absorption of the CO₂. However, these ILs were still limited to a 1:2 mol of CO₂ per mole of IL ratio, denoted $n\text{CO}_2/n\text{IL}$. It was then reported that by adding an amine moiety to both the anion and the cation equimolar CO₂ capture could be reached.¹² Gurkan et al.¹³ showed that, by selecting an amino acid anion-based IL such as the trihexyl-tetradecylphosphonium proline, [P₆₆₆₁₄][Pro], a 1:1 stoichiometry could be reached at room temperature and atmospheric pressure. Although these ILs showed high CO₂ capacity, their

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high viscosity after CO₂ solvation made them unsuitable for a practical industrial application. This change in viscosity is mainly due to the formation of strong hydrogen-bonded networks resulting in an increase of the overall cohesive energy of the solution in the presence of CO₂.¹⁴ Luo et al.¹⁵ showed that a high absorption capacity up to 1.6 mol of CO₂ per mole of IL could be reached by using pyridine containing anion functionalized ILs. The highest value reported (1.6 mol of CO₂ per mole IL) was found using a 4-azabenzimidazole-based IL [P₆₆₆₁₄][4-ABI] at 20 °C and 1 atm. The group also reported these ILs to be recyclable with no loss in absorption after 6 cycles using a desorption temperature of 80 °C.

Recently, a range of superbase ILs have been reported which showed efficient and reversible CO₂ capture with an uptake greater than the 1:1 nCO₂/nIL.^{16–18} Unlike the amino acid-based ILs, these ILs have a limited number of hydrogen atoms on the anion and, therefore, only a small increase in viscosity upon CO₂ absorption is observed. In addition, as flue gas/methane streams contain water it is also important to understand how these ILs behave under wet conditions. The presence of water has been shown to affect the physical properties of the IL and also has the potential to compete with the CO₂ for absorption.^{18,19} Using the trihexyl-tetradecylphosphonium cation, [P₆₆₆₁₄]⁺, paired with a range of superbasic anions, including 1,2,3-triazolide ([123Triz][−]), 1,2,4-triazolide ([124Triz][−]), phenoxide ([PhO][−]), benzotriazolide ([Bentriz][−]), and benzimidazolide ([Benzim][−]), work within our laboratory has shown that the presence of water can have a positive or negative effect on the CO₂ uptake depending on the anion structure.¹⁸ Where the effect was detrimental the change was small, for example in the case of [P₆₆₆₁₄][124Triz] a decrease from 0.92 nCO₂/nIL under dry conditions to 0.89 nCO₂/nIL under wet conditions was observed at 295.15 K and atmospheric pressure. However, it was also shown that the presence of water could enhance the CO₂ absorption in some superbase ILs, with an increase from 0.26 to 0.63 or from 0.35 to 0.86 nCO₂/nIL observed in the case of the [Bentriz][−] or [123Triz][−] based IL under dry and wet conditions at 295.15 K and atmospheric pressure, respectively. Furthermore, as expected, under wet conditions, the viscosity of these ILs before and after CO₂ absorption is much lower than that under dry conditions, showing that these ILs are more promising solvents for industrial application. NMR studies carried out showed that the CO₂ competes effectively with water for CO₂ absorption.^{18,20} The studies also showed that the [124Triz][−] based IL retained 97% of its CO₂ capacity under wet conditions over six cycles showing that CO₂ absorption is recyclable and suggesting that the water does not have an irreversible effect on the CO₂ uptake.¹⁸

In recent years, solutions of alkanolamine and IL mixtures have also been investigated for their CO₂ capture capabilities. Reports have shown these mixtures could help overcome drawbacks associated with the current technology.^{21–28} Camper et al.²¹ studied mixtures of pure MEA and [C₆mim][NTf₂]. Therein, the CO₂ solubility was found to approach 0.5 mol of CO₂ per mole of amine and suggests that these mixtures may reduce the energy of desorption in comparison with the aqueous alkanolamine solution. Other studies have reported that a mixture of MEA and the 1-butyl-3-methylimidazolium tetrafluoroborate, [C₄mim][BF₄] could give a higher capacity reaching 0.638 mol CO₂ per mole of MEA and better regeneration than that of a pure amine system.²² Another study reported by Yang et al.²³ showed the advantage of adding

an IL, such as the [C₄mim][BF₄], to an aqueous amine solution in order to enhance its CO₂ solubility. During this study, these authors showed that the mixture based on 30 wt % MEA + 40 wt % [C₄mim][BF₄] + 30 wt % H₂O had a 37.2% lower energy consumption than that of a standard aqueous amine solution. Zhang et al. also found that the addition of the methyldiethanolamine (MDEA) could increase the rate and the CO₂ capacity in tetramethylammonium glycinate, [N₁₁₁₁][Gly].^{24–26} During this work, this group showed that the aqueous mixture based on 15 wt % [N₁₁₁₁][Gly] + 15 wt % MDEA reaching a capacity of 0.64 nCO₂/namine in less than 100 min. Zhao et al.²⁷ investigated the performance of CO₂ in 16 different absorbents including (amine + IL + H₂O), (IL + H₂O), and (amine + H₂O) systems as a function of the composition and temperature (from 303.15 to 343.15 K) and at 1.50 MPa. These solutions also present a viscosity lower than 17.00 mPa·s at room temperature, which is much lower than that of the pure ILs studied, which is an advantage for a practical application. Therein, it was also reported that the (monodiethanolamine + 2-2[hydroxyethyl(methyl)amino]-ethanol chloride + water + piperazine) solution had a large CO₂ capacity close to 0.158 in CO₂ weight fraction. A more recent study on the aqueous 1-hydroxyethyl-3-methylimidazolium glycinate, [C₂OHmim][Gly], and MEA mixtures showed an optimum composition of 0.7 mol·dm^{−3} MEA and 0.3 mol·dm^{−3} of IL with a capacity of 0.534 nCO₂/nabsorbent and suggested that the components mutually promote the CO₂ solubility. Furthermore, this particular system showed good stability and CO₂ uptake and release as a capacity of 0.480 nCO₂/nabsorbent was still observed after the fourth cycle.²⁸ These recent studies have shown that these mixtures can reduce the viscosity of the ILs and decrease absorption time with maximum absorption being reached in 60 min in some cases.^{26,27,29} It was also shown that they can reduce the loss of material and energy consumption associated with current amine technology.^{21–23} This solution presents itself as an attractive method to utilize the performance of amines while using the desirable properties of ILs.

In this study MEA was added to the previously studied superbase ILs to investigate the effect of a chemically absorbing cosolvent compared with our previous work with water as a nonreacting cosolvent.¹⁷ As noted, water can have a positive influence on the CO₂ solubility in superbase ILs which is thought to be partly due to the formation of OH[−] on reaction with the superbase. Herein, the CO₂ solubility in five superbase IL/MEA systems is reported at 295.15 K and atmospheric pressure to examine the influence of a molecule containing both an −OH group as well as the reactive −NH₂ in order to explore whether a synergistic effect could be obtained. Few studies have examined similar reactive systems and this also has the potential to reduce the volatility of the MEA which is a major problem in the current aqueous MEA solutions utilized industrially. Furthermore, no CO₂ solubility data in binary mixtures containing a superbase IL and the pure MEA has been reported, to date. Five superbase ILs, namely the trihexyl-tetradecylphosphonium ([P₆₆₆₁₄]⁺) cation paired with anions [123Triz][−], [124Triz][−], [Bentriz][−], [Benzim][−], and [Im][−] were selected due to their high CO₂ capture capacity even under wet conditions.¹⁸ Their CO₂ capacity, viscosity data before and after CO₂ uptake as a function of the MEA concentration as well as the recyclability of the system has been reported and compared with an analogous nonreactive ionic liquid based on the bis[(trifluoromethyl)sulfonyl]imide

([NTf₂][−]) anion. In addition, the effects of MEA vs water addition to the superbase ILs are compared.

2. EXPERIMENTAL SECTION

2.1. Materials and Superbase ILs Synthesis. With the exception of [P₆₆₆₁₄]Cl which was obtained from Cytec (98%) and lithium bis[(trifluoromethyl)sulfonyl]imide (LiNTf₂) which was purchased from 3 M (>98%), all IL precursors were purchased from Sigma-Aldrich, including 1,2,4-triazole (98%), benzotriazole (99%), 1,2,3-triazole (97%), benzimidazole (98%), imidazole (99%). Gaseous nitrogen (99.998%) and carbon dioxide (99.99%) were obtained from BOC and passed through drying columns before being contacted with the IL/MEA samples. The water was purified using a Milli-Q 18.3 MΩ water purification system. Deuterated chloroform-d (CDCl₃) and dimethyl sulfoxide-d₆ (DMSO) were obtained from Sigma-Aldrich within a purity close to 99.8 atom % D and 99.9 atom % D, respectively. Monoethanolamine (99%) was obtained from Sigma-Aldrich. This was distilled under vacuum at 353 K and stored in an argon filled dry glovebox. The superbase ILs were prepared using a two-step synthesis described previously.¹⁸

[P₆₆₆₁₄][NTf₂] was synthesized from [P₆₆₆₁₄]Cl (50.8 g, 0.098 mol) dissolved in dichloromethane 100 cm³ and added dropwise to Li[NTf₂] (28.7 g, 0.1 mol) dissolved in ultrapure water (100 cm³) and allowed to stir at room temperature overnight. The organic layer was then extracted and washed with ultrapure water (100 cm³) repeatedly five times and dried under high vacuum.

All ILs were then dried under high vacuum (1 Pa at 50 °C) and then stored in an argon filled dry glovebox prior to use.

Name, source, and initial and final purity of compounds used during this work are listed in Table S1 of the [Supporting Information](#).

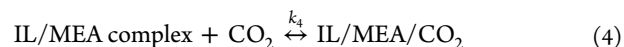
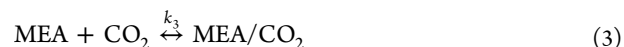
2.2. Methods. The purity of the synthesized ILs and IL/MEA mixtures were analyzed using ¹H NMR using a Bruker Avance 400 MHz Ultra shield Plus NMR spectrometer as reported in Figure S1 of the [Supporting Information](#) and a 300 MHz Ultra shield Plus NMR spectrometer, respectively. In each case, the NMR experiments were carried out neat in the presence of a glass capillary insert containing deuterated solvents (CDCl₃ or DMSO). The quantity and solubility limit of MEA in the mixture was determined using ¹H NMR at 295.15 K. The water content of the investigated systems were measured using a Metrohm 787 KF Titrino Karl Fischer titrator and was lower than 0.1 wt % for all ILs investigated and close to 0.013 wt % for the MEA after distillation, while a water level up to 1.1 wt % was observed in the case of IL/MEA mixtures.

The viscosity of the IL samples was measured before and after CO₂ absorption using a cone and plate Bohlin Gemini Rotonetic Drive 2 viscometer. The temperature in the cell was regulated at (298.15 ± 0.01) K using an in-built precise Peltier thermostat. The viscosity standard (ASTM Oil Standard S600 of CANNON, 1053 mPa·s at 298.15 K) and ultrapure water were used to calibrate the viscometer. On the basis of these measurements, the accuracy of the reported viscosity measurements is close to ±1%. The biphasic system resulting from the addition of water to the IL/MEA mixtures was analyzed by ¹H NMR after 1 h of stirring and settling time at 295.15 K.

2.3. CO₂ Absorption and Desorption Experiments. All samples were prepared, stored, and weighed out into a small vial with a septum lid (1.9 cm³) in an argon filled glovebox. The absorption measurements of the pure and water saturated

systems were described in a previous work.¹⁸ The measurement of the CO₂ uptake in the IL/MEA mixtures followed the same gravimetric procedure. The sample (~0.5 g) was pretreated by bubbling with dry nitrogen at 353 K for 1 h (50 cm³·min^{−1}) at 313.15 K and the weight of the sample was recorded on an electronic balance with an accuracy of ±0.1 mg. In addition, the loss of MEA during this pretreatment was determined via ¹H NMR spectroscopy. The sample was then bubbled with CO₂ (50 cm³·min^{−1}) at room temperature (295.15 ± 0.5 K) for the required period of time, and the weight gain was used to calculate the amount of CO₂ absorbed considering the mole fractions of each component (taking into account the mass of the headspace). The CO₂ absorption was monitored at intervals of 5, 15, 30, and 60 min. For desorption of CO₂, the sample was bubbled with N₂ (50 cm³·min^{−1}) at 353.15 ± 0.5 K for 120 min. A desorption experiment was also carried out at 393.15 ± 0.5 K for 60 min. The MEA loss during desorption was quantified by ¹H NMR and the additional MEA needed to restore an equimolar system was calculated and added prior to the CO₂ being reabsorbed, as described above.

2.4. Equilibrium Constant for IL/MEA System. The equilibrium constant for investigated [P₆₆₆₁₄][Bentriz]/MEA mixtures at varying mole ratios were calculated based on the following four reactions:



where k_i is equilibrium constant of the reaction i (with $i = 1, 2, 3$, or 4).

To solve this problem, several assumptions have been made, such as (i) the formation of the IL/MEA complex is driven by an 1:1 molar ratio (eq 1); (ii) the solubility of the CO₂ in free IL was calculated on the basis of a 1:0.23 mol of IL per mole of CO₂ ratio based on experimental data for the pure IL system (eq 2); (iii) the solubility of the CO₂ in free MEA was determined on the basis of a 1:0.42 mol of MEA per mole of CO₂ ratio based on experimental data for the pure MEA system; (iv) the solubility of the CO₂ in the IL/MEA complex was assumed to follow a 1:1 mol of IL/MEA complex per mole of CO₂ ratio.

Equation 5 was then used to calculate the equilibrium constant k_1 (eq 1).

$$K = \frac{x}{(1-x)^2} \quad (5)$$

where k_1 is the equilibrium constant of the eq 1 and x defines the number of moles of IL/MEA complex formed on the basis of an 1:1 molar ratio.

This equilibrium constant was then calculated using solver within Microsoft Excel using the overall mass balances for the CO₂, IL, and MEA as boundary conditions and a constant value of k_1 as the convergence criterion across all data. The accuracy was tested against experimental values of CO₂ uptake in [P₆₆₆₁₄][Bentriz]/MEA molar ratios of 1:3, 1:1, and 3:1 mol of IL per mole of MEA resulting in a RAAD of 13% in mole fraction units which is within the error of the experimental data.

3. RESULTS AND DISCUSSION

3.1. MEA Miscibility in Selected Superbase ILs. Prior to the determination of the CO₂ solubility in the selected (IL + MEA) mixtures, the miscibility of MEA in each IL was determined at 295.15 K by using ¹H NMR spectroscopy. As shown in Table 1, the MEA is only partially miscible in each

Table 1. MEA Solubility Expressed in MEA Weight Fraction, w_{MEA} , in the Selected ILs at 295.15 K and Atmospheric Pressure along with the Water Content (wt%) in Each Equilibrium Mixture^a

ionic liquid	water content (wt %)	w_{MEA}
[P ₆₆₆₁₄][124Triz]	< 0.8	0.379
[P ₆₆₆₁₄][123Triz]	< 0.6	0.409
[P ₆₆₆₁₄][Bentriz]	< 0.2	0.325
[P ₆₆₆₁₄][Benzim]	< 0.8	0.261
[P ₆₆₆₁₄][Im]	< 0.9	0.316
[P ₆₆₆₁₄][NTf ₂]	< 0.04	0.203

^a $u(\text{water content}) = (0.01 \times \text{water content}) \text{ wt \%}$; $u(w_{\text{MEA}}) = 0.001$; $u(T) = 0.5 \text{ K}$.

selected IL. The MEA solubility in the five ILs, expressed in MEA weight fraction unit, ranged from 0.26 to 0.41. MEA was the most soluble in [P₆₆₆₁₄][123Triz] with a $w_{\text{MEA}} = 0.41$ and it then decreased in the following order: [P₆₆₆₁₄][124Triz] > [P₆₆₆₁₄][Bentriz] > [P₆₆₆₁₄][Im] > [P₆₆₆₁₄][Benzim] > [P₆₆₆₁₄][NTf₂] with a $w_{\text{MEA}} = 0.20$. The high solubility reflects a strong interaction between MEA and the anion through N...H...O hydrogen bonds.³⁰ From data reported in Table 1, it is clear that, the solubility of MEA is higher in triazolide-based ILs than the imidazolide-based ILs which may be associated with the potential for the -OH, for example, to hydrogen bond in a bidentate structure across two adjacent nitrogens and, as a result, becomes more stable in the former ILs. The decrease in the MEA solubility for those anions with an additional aromatic system, that is, [P₆₆₆₁₄][Bentriz] and [P₆₆₆₁₄][Benzim], suggests that the anion-anion interactions through, for example, increased π - π stacking significantly affect the MEA solvation process in these superbase ILs. As reported in Table 2, the water solubility in the selected ILs decreases in the following order: [P₆₆₆₁₄][Im] = [P₆₆₆₁₄][123Triz] > [P₆₆₆₁₄][124Triz] > [P₆₆₆₁₄][Benzim] > [P₆₆₆₁₄][Bentriz]. The water solubility in these ILs was found to range typically from 0.07 to 0.12 in

water weight fraction units at 295.15 K (Table 2) showing that the MEA is more soluble in these superbase ILs than the water. Investigations were also performed on the three-component system (IL + MEA + water). In this case, even at low concentrations of water, a biphasic system was obtained with the aqueous phase containing more than 90% of the MEA. This was demonstrated by adding 0.6 g of H₂O into 0.5 g of a mixture containing an equimolar amount of [P₆₆₆₁₄][Bentriz] and MEA at 295.15 K. In this case, the water layer contained 0.00074 mol (i.e., 91.4%) of MEA while 0.00007 mol (i.e., 8.6%) of MEA was present in the IL layer. Due to this effect, only the binary mixtures were examined for CO₂ capture, hereafter.

3.2. CO₂ Solubility. The CO₂ solubility in the five superbase IL and MEA absorbents was determined using a gravimetric method at atmospheric pressure and room temperature (e.g., 295.15 \pm 0.5 K). Initially the volatility of the MEA in the mixture was determined via ¹H NMR spectroscopy, that is, by assessing the quantity of MEA lost during the initial pretreatment of the mixture. This allows for a more accurate representation of the CO₂ capture ability. The mol % loss is shown in Table S2 of the Supporting Information.

The effect of the presence of MEA on the CO₂ solubility in the selected superbase ILs is shown in Table 2 and Figure 1.

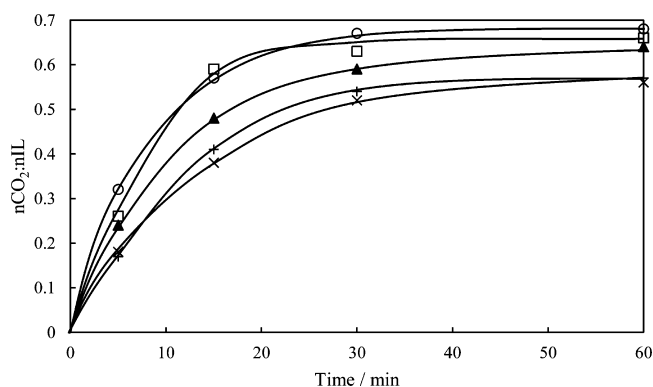


Figure 1. CO₂ absorption in the investigated equimolar (IL + MEA) mixtures as a function of time in [P₆₆₆₁₄][Im] (□), [P₆₆₆₁₄][124Triz] (○), [P₆₆₆₁₄][Bentriz] (×), [P₆₆₆₁₄][123Triz] (+), and [P₆₆₆₁₄][Benzim] (Δ).

Table 2. Comparison of the CO₂ Solubility in Pure ILs (Dry Conditions), Water Saturated ILs (Wet Conditions) and of the Investigated Equimolar (IL + MEA) Mixtures^a

ionic liquid	CO ₂ absorption after 1 h—corresponding to the equilibrium							
	pure IL		absorption under wet conditions			absorption in equimolar (IL + MEA) mixture		
	water content before CO ₂ absorption (wt %)	$n\text{CO}_2/n\text{IL}$	water content after saturation with water and CO ₂ (wt %)	$n\text{CO}_2/n\text{IL}$	$n\text{CO}_2/n_{\text{absorbent}}$	$n\text{CO}_2/n_{\text{absorbent}}$	theoretical ideal	$n\text{CO}_2/n\text{IL}$
[P ₆₆₆₁₄][124Triz]	0.046	0.92	11.27	0.84	0.20	0.68	0.69	1.23
[P ₆₆₆₁₄][123Triz]	0.078	0.35	11.57	0.76	0.19	0.58	0.38	1.06
[P ₆₆₆₁₄][Bentriz]	0.042	0.23	7.42	0.60	0.19	0.56	0.31	1.08
[P ₆₆₆₁₄][Benzim]	0.075	1.06	8.42	0.91	0.23	0.65	0.74	1.30
[P ₆₆₆₁₄][Im]	0.019	0.83	11.59	0.88	0.20	0.65	0.63	1.25

^aHerein, reported CO₂ absorption data, carried out at 295.15 K and 0.1 MPa, are considered as equilibrium properties. Where $n\text{CO}_2/n_{\text{absorbent}}$ data represents the moles of CO₂ absorbed per the total number of moles of absorbents: i.e., including superbase IL, water and/or MEA, while $n\text{CO}_2/n\text{IL}$ data consider only the number of mole of IL in each solution. $u(\text{water content}) = (0.01 \times \text{water content}) \text{ wt \%}$; $u(n\text{CO}_2/n_{\text{absorbent}}) = 0.01$; $u(T) = 0.5 \text{ K}$; $u(P) = (0.01 \times P) \text{ MPa}$.

These results show that, for a 1:1 mol ratio of IL/MEA, [P₆₆₆₁₄][124Triz] has the highest capacity with a value of 0.68 nCO₂/nabsorbent at 295.15 K and 0.1 MPa. Absorption capacities then decrease for the mixtures in the following order: [P₆₆₆₁₄][124Triz] > [P₆₆₆₁₄][Benzim] = [P₆₆₆₁₄][Im] > [P₆₆₆₁₄][123Triz] > [P₆₆₆₁₄][Bentriz]. Comparing these CO₂ capacities with those of the pure ILs (see Table 2) it is observed that the presence of MEA in solution can have a detrimental effect on the CO₂ capture ability of these superbase ILs. For example, the CO₂ capacity in [P₆₆₆₁₄][124Triz] decreased from 0.92 nCO₂/nIL to 0.68 nCO₂/nabsorbent in the presence of MEA (1:1 mol ratio). A similar trend was also followed for the [P₆₆₆₁₄][Benzim] and [P₆₆₆₁₄][Im]. Interestingly, the results show that, in the case of the [P₆₆₆₁₄][123Triz] and [P₆₆₆₁₄][Bentriz], the presence of MEA in solution enhanced the CO₂ capacity. For [P₆₆₆₁₄][123Triz], the capacity increased from 0.35 nCO₂/nIL for the pure IL to 0.58 nCO₂/nabsorbent for the equimolar (IL + MEA) mixture. Similarly, for [P₆₆₆₁₄][Bentriz], its CO₂ capacity increased from 0.23 nCO₂/nIL to 0.56 nCO₂/nabsorbent by adding an equimolar amount of MEA in solution. These values may be compared with previously reported studies using [C₂OHmim][Gly] in an aqueous blend with MEA for CO₂ capture. The highest value reported for this system by Lv et al. was 0.534 using a mixture of 0.7 mol·dm⁻³ MEA and 0.3 mol·dm⁻³ IL.²⁸ Increased values for CO₂ capture are found in this study in comparison.

The trends observed on the addition of MEA to the superbase ILs is similar to the previously reported results when these superbase ILs were tested for their CO₂ capacity after saturation with water at 295.15 K (Table 2).¹⁸ Again, both [P₆₆₆₁₄][123Triz] and [P₆₆₆₁₄][Bentriz] exhibited an enhancement in the presence of water whereas a decrease was obtained for [P₆₆₆₁₄][124Triz], [P₆₆₆₁₄][Benzim] and [P₆₆₆₁₄][Im] ILs. The fact that for both a reactive and a nonreactive additive similar trends are observed may indicate that it is not solely due to interaction of the CO₂ with the MEA or water but also due to the availability of the anion for CO₂ interaction. Upon comparison it would appear that these solvents have a similar effect on the ILs tested whether this is an enhanced or undesirable effect on the CO₂ uptake of the pure superbase ILs. As water acts as a nonreactive solvent and MEA is a solvent that chemically binds with the CO₂ it is difficult to accurately compare the two. As a result comparing the CO₂ absorption under wet conditions in terms of nCO₂/nabsorbent shows that water is not as evidently beneficial for CO₂ absorption as it initially could appear with the [P₆₆₆₁₄][123Triz] giving 0.19 nCO₂/nabsorbent after saturation with water compared to 0.58 nCO₂/nabsorbent in an equimolar ratio with MEA.

Table 3 shows the CO₂ absorption in terms of the mass of CO₂ absorbed in the pure IL, the water saturated ILs, and 1:1 mol ratio IL/MEA systems displayed as wt %. To evaluate the potential industrial application of these systems, it is useful to consider the CO₂ uptake in terms of mass of absorbent: higher wt % CO₂ will result in a lower overall cost of the system. As can be seen, the IL/MEA mixtures provide the highest absorption in terms of mass, with the highest found for the [P₆₆₆₁₄][124Triz] IL at 9.7 wt % of CO₂. In general, water saturation also led to an increase in the wt % CO₂ absorption capacity with ~7 wt % found for [P₆₆₆₁₄][124Triz], [P₆₆₆₁₄][Benzim], and [P₆₆₆₁₄][Im]; however, only ~2 wt % was observed for the analogous wet [123Triz]⁻ and [Bentriz]⁻ based ILs. For the pure ILs the CO₂ capacity was in the range 4–6 wt %. Figure 2 shows the comparison of the pure IL and

Table 3. CO₂ Absorption in Superbase IL-Based Solutions Reported in wt %^a

ionic liquid	wt % of CO ₂ in absorbent		
	pure IL	wet conditions	IL/MEA (1:1)
[P ₆₆₆₁₄][124Triz]	5.70	7.24	9.66
[P ₆₆₆₁₄][123Triz]	5.84	2.91	8.29
[P ₆₆₆₁₄][Bentriz]	4.14	2.07	7.26
[P ₆₆₆₁₄][Benzim]	5.68	7.83	8.98
[P ₆₆₆₁₄][Im]	5.94	6.54	9.33

^aHerein, reported CO₂ absorption data, carried out at 295.15 K and 0.1 MPa, are considered as equilibrium properties in the case of the pure ILs (dry conditions), water saturated ILs (wet conditions) and of the investigated equimolar (IL + MEA) mixtures. $u(\text{wt \%CO}_2) = 0.05$; $u(T) = 0.5 \text{ K}$; $u(P) = (0.01 \times P) \text{ MPa}$.

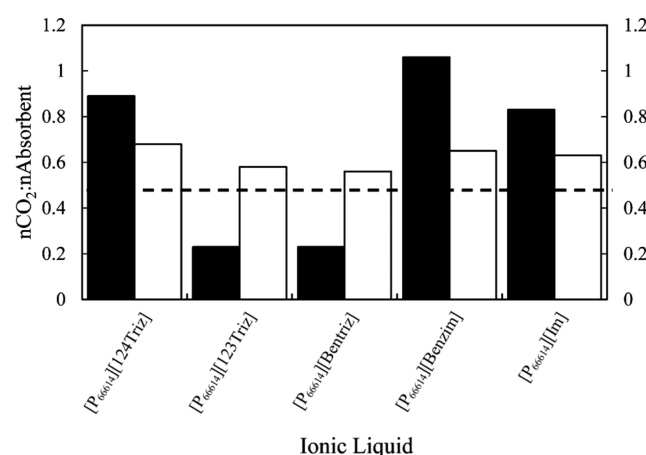


Figure 2. Comparison of CO₂ absorption in pure ILs (■) and in equimolar (IL + MEA) mixtures (□) with the current industrial benchmark for CO₂ capture (2:1 nCO₂/namine) represented by the dashed line.

equimolar IL/MEA systems with the industrial benchmark for CO₂ capture process. It shows that each of these systems gives a better CO₂ capacity than the aqueous amine system currently implemented.

3.3. Viscosity. Previous studies^{27–29} have shown that the addition of MEA to IL reduces the viscosity issues associated with the pure ILs for CO₂ uptake, for example. The viscosities of equimolar (superbase IL + MEA) mixtures were measured at 298.15 K before and after CO₂ solvation as reported in Table 4.

Table 4. Physical Properties of Investigated Equimolar (IL + MEA) Mixtures at 298.15 K and Atmospheric Pressure Including Water Content and Viscosity (η) before and after CO₂ Absorption^a

ionic liquid	water content (wt %)	viscosity (mPa·s)	
		before CO ₂	after CO ₂
[P ₆₆₆₁₄][124Triz]	0.78	169	1315
[P ₆₆₆₁₄][123Triz]	0.54	154	806
[P ₆₆₆₁₄][Bentriz]	0.14	197	1174
[P ₆₆₆₁₄][Benzim]	0.84	336	1286
[P ₆₆₆₁₄][Im]	1.10	168	863
[P ₆₆₆₁₄][NTf ₂]	0.04	90	229

^a $u(\text{water content}) = (0.01 \times \text{water content}) \text{ wt \%}$; $u(\eta) = (0.01 \times \eta) \text{ mPa}\cdot\text{s}$; $u(T) = 0.01 \text{ K}$.

The results confirm that, prior to the treatment with CO₂, the viscosity of all the ILs investigated are lower when MEA is present in solution compared with the pure IL, as expected. For example, the viscosity of the pure [P₆₆₆₁₄][124Triz] decreased from 569 mPa·s to 169 mPa·s by adding an equimolar amount of MEA. The viscosities are found to decrease in the order [P₆₆₆₁₄][Benzim] > [P₆₆₆₁₄][124Triz] > [P₆₆₆₁₄][123Triz] > [P₆₆₆₁₄][Bentriz] > [P₆₆₆₁₄][NTf₂] for the pure ILs (Table S3) and [P₆₆₆₁₄][Benzim] > [P₆₆₆₁₄][Bentriz] > [P₆₆₆₁₄][123Triz] > [P₆₆₆₁₄][124Triz] ≥ [P₆₆₆₁₄][Im] > [P₆₆₆₁₄][123Triz] > [P₆₆₆₁₄][NTf₂] for the 1:1 IL/MEA mixtures. Interestingly, unlike the results found for the pure ILs, upon absorption of CO₂ into the IL/MEA mixtures a large increase in viscosity is observed. The largest increase was observed for the equimolar [P₆₆₆₁₄][124Triz]/MEA system with a viscosity change from 167 mPa·s before CO₂ absorption to 1315 mPa·s after CO₂ absorption. This is unlike the pure IL in which CO₂ absorption resulted in only a small increase in viscosity.¹⁸ Similar increases in viscosity upon CO₂ sorption were also reported by Fu et al.,³¹ wherein, for a mixture of 0.35 wt_{MDEA}/0.15 wt_{[Bmim][Gly]} in water, the viscosity increased from 6.59 mPa·s to 10.35 mPa·s upon the addition of CO₂. The addition of MEA had a similar effect on the viscosity to the addition of water as was previously reported (Table S3), that is, a decrease was observed in both cases. However, a much greater change in viscosity was observed upon CO₂ absorption in the equimolar (IL + MEA) systems compared with the wet IL systems. In the latter, only a small increase in viscosity from 114 to 200 mPa·s was found on absorbing CO₂ into the water saturated [P₆₆₆₁₄][124Triz], for example. This difference in viscosity between the MEA and water cosolvents after CO₂ absorption is expected due to the reactive nature of the MEA in the presence of CO₂ leading to an increase of ions in solution. This induces an increase of the Coulombic interactions in solution affecting the cohesive energy of the solution.

This increase in viscosity on CO₂ absorption for the equimolar (IL + MEA) systems is important as it has been reported widely that the presence of an amine in ILs leads to enhanced kinetics of absorption over the pure IL, in the case of nonreactive ILs.¹ Viscosity data for (reactive IL + MEA) systems after CO₂ uptake is not widely reported in the literature and is an important factor to consider for an industrial application. The large increase in viscosity observed in the equimolar (superbase IL + MEA) systems following CO₂ absorption demonstrates that this may be a significant limitation for industrial application. It should be noted, as reported in the Table S3, that a small increase in viscosity has been generally observed in the case of the selected superbase ILs in the absence and presence of water and this should be examined for other potential IL systems. Figure 3 compares the absorption kinetics for the pure IL, (water + IL) at the water saturation level and equimolar (IL + MEA) systems for the case of [P₆₆₆₁₄][124Triz] as represented as % of the saturation number of moles of CO₂ absorbed with respect to time (Table S4). No significant differences were observed for the three systems studied suggesting that the rate of absorption of CO₂ is not just dependent on the viscosity. This is further demonstrated in Figure 4 as no correlation was found by fitting the viscosity of the equimolar (IL + MEA) mixtures before the CO₂ uptake as the function of their initial rate of CO₂ uptake. This indicates that mass transfer of CO₂ is not rate determining for the uptake and, therefore, it is likely due to the

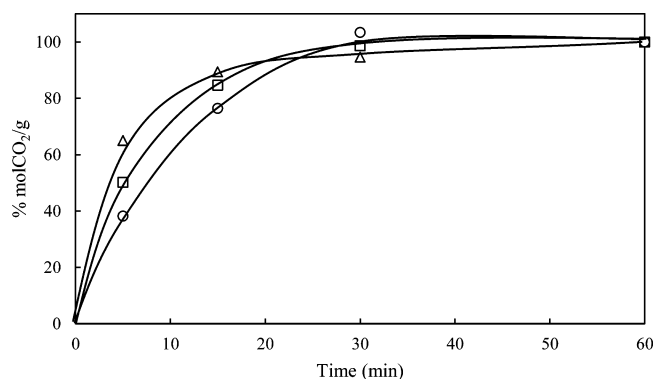


Figure 3. Comparison of the % of moles of CO₂ (normalized per weight of the absorbing solution) as a function of time for [P₆₆₆₁₄][124Triz] as the pure IL (Δ), water saturated (\circ) and in solution with MEA (equimolar binary mixture) (\square).

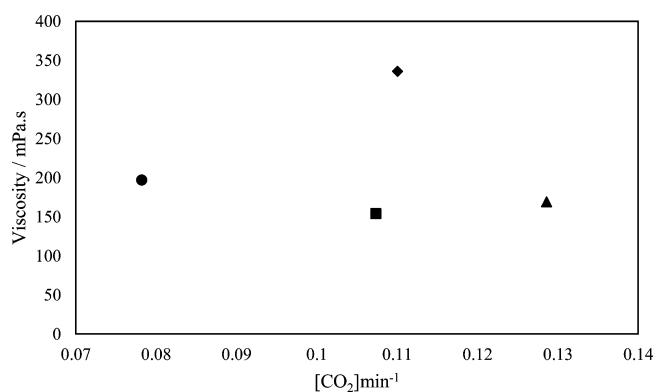


Figure 4. Comparison of initial viscosities of investigated equimolar (IL + MEA) mixtures. [P₆₆₆₁₄][Bentriz] (\bullet), [P₆₆₆₁₄][123Triz] (\blacksquare), [P₆₆₆₁₄][124Triz] (\blacktriangle) and [P₆₆₆₁₄][Benzim] (\blacklozenge) with the initial rate of CO₂ absorption.

structure of the system and varying strengths of interaction between the ion pairs also playing a significant role.

3.4. Synergy between the IL and MEA Components.

The five equimolar (IL + MEA) mixtures were probed to investigate their synergistic properties. That is, are the components of the absorbent working together to increase the CO₂ capture ability or are the two components working independently to absorb CO₂. In Table 2, the calculated ideal results are displayed, using a capacity of 0.42 nCO₂/nabsorbent for the MEA component and the experimental values obtained previously for the pure ILs.¹⁸ A comparison of the ideal and experimental results for the [124Triz]⁻ based IL with MEA in an equimolar ratio shows an experimental value of 0.68 nCO₂/nabsorbent versus a theoretical value of 0.69 nCO₂/nabsorbent, suggesting that this acts as an ideal system, that is, the CO₂ capacity is a weighted average of the two individual capacities for the IL and MEA. This is also found using the [P₆₆₆₁₄][Benzim] and [P₆₆₆₁₄][Im] ILs.

In comparison, for the [P₆₆₆₁₄][123Triz] and [P₆₆₆₁₄][Bentriz] ILs an increase in the overall absorption capacity is observed compared with the ideal case, Figure 5 shows the CO₂ uptake as a function of IL/MEA mole ratio for the [P₆₆₆₁₄][Bentriz]. The dashed line is representative of the ideal CO₂ uptake and demonstrates that at all compositions of IL/MEA tested [P₆₆₆₁₄][Bentriz] and MEA behave in a synergistic manner with enhanced CO₂ solubility compared

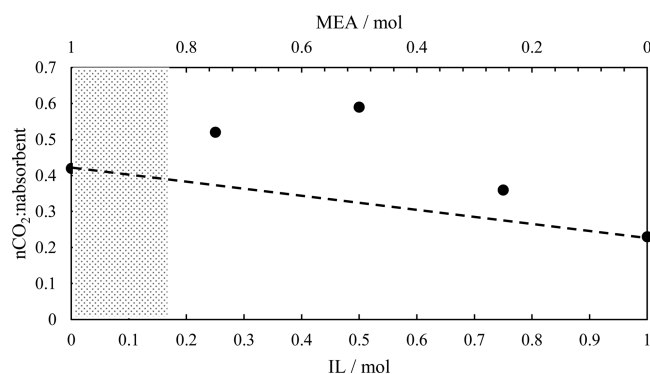


Figure 5. Comparison of CO₂ capture ($n_{\text{CO}_2}/n_{\text{absorbent}}$) as a function of [P₆₆₆₁₄][Bentriz]/MEA mole ratio at 295.15 K and 0.1 MPa. The dashed line represents the expected ideal uptake of CO₂ under these conditions. The shaded area represents the solubility limit of MEA in [P₆₆₆₁₄][Bentriz] at 295.15 K and 0.1 MPa.

with the ideal case. Figure 5 also shows that the highest synergy is achieved at the 0.5:0.5 IL/MEA ratio. Using these solubility data and the mathematical model described in section 2.4, the equilibrium constant k_1 was then calculated. A very high value for the equilibrium constant k_1 , close to 4190, was obtained upon modeling the data, which suggests that the [P₆₆₆₁₄]-[Bentriz] and MEA react forming a strongly bound complex. Therefore, the enhanced CO₂ sorption in this binary mixture is associated with the complex formed plus the contribution from the remaining free IL or MEA, depending on which is in excess. A similar effect was recently reported by Lv et al.²⁸ studying an aqueous solution containing the [C₂OHmim][Gly] and the MEA, suggesting that in this case both the IL and MEA react with the CO₂ through the formation of a zwitterion, which leads to the IL and MEA competing for CO₂ absorption and so an enhancement in capture. This synergistic effect discussed is an added benefit from the addition of MEA to these superbase ILs. The effect is not widely discussed in literature with many groups reporting the reduction in viscosity when an amine is present as a main advantage of these systems for CO₂ capture.^{24–26}

A comparison of these systems was also performed with a physically absorbing IL (e.g., [P₆₆₆₁₄][NTf₂]). Due to the weak hydrogen bonding capability of the [NTf₂][−] anion the MEA forms a much weaker interaction with the IL compared with the superbase ILs and, therefore, its volatility is very high. For example, during the gas absorption process, significantly increased levels of MEA loss of close to 50 mol % were found after 60 min in this system compared with only <8 mol % loss from ILs containing the superbasic anion. In addition, the [P₆₆₆₁₄][NTf₂] only has an absorption capacity of 0.04 leading to very large increases in absorption upon the addition of MEA. Such a large difference leads to significant errors in assessing any synergy between the components.

The enhanced CO₂ capture observed suggests that the CO₂ competes effectively with the −OH group on the MEA to reprotonate the anion and both the IL and MEA components chemically absorbing the CO₂. This is similar to what was reported in the previous work in which the H₂O is also seen to compete effectively with the CO₂.¹⁸ It is likely that this is an entropy driven reaction and the presence of a cosolvent causes a weakening of the interaction between the anion and cation giving the CO₂ greater opportunity for interaction with the anion of the IL, as noted for the system in the presence of

water.¹⁸ It was reported previously that the H₂O disrupts the anion–cation interaction in which an enhancement was observed allowing increased interaction of the anion with CO₂. In general, this occurs for the anions which have low CO₂ solubility in the pure IL system. It is therefore possible that the MEA acts in a similar manner although in this case a stable complex is formed which is unlikely to be the case in the H₂O containing system.

3.5. Desorption and Regeneration. Regeneration tests were carried out using an equimolar [P₆₆₆₁₄][Bentriz]/MEA mixture at desorption temperatures of 353.15 and 393.15 K. As shown in Table 5 it was found that at 353.15 K, the CO₂

Table 5. Comparison of Recyclability of Equimolar ([P₆₆₆₁₄][Bentriz] + MEA) Mixture after CO₂ Desorption at 353.15 and 393.15 K^a

CO ₂ absorption test	353.15 K		393.15 K	
	$n_{\text{CO}_2}/n_{\text{absorbent}}$	theoretical ideal	$n_{\text{CO}_2}/n_{\text{absorbent}}$	theoretical ideal
1	0.51	0.31	0.51	0.22
2	0.42	0.32	0.49	0.23
3	0.24	0.33	0.42	0.27

$$^a u(n_{\text{CO}_2}/n_{\text{absorbent}}) = 0.01; u(T) = 0.5 \text{ K.}$$

capacity decreased by 47% after three cycles and no synergistic effect was observable. This is thought to occur because at this temperature not all of the CO₂ has been removed, which reduces the number of active sites for CO₂ capture. When the temperature of desorption was increased to 393.15 K, it can be seen that the CO₂ absorption capacity decreased slightly, but even after three cycles a significant synergistic effect was observable. After desorbing CO₂ at 393.15 K it is necessary to add an average of 3.84 wt % MEA to restore an equimolar system. However, the amount of fresh MEA needed in the system could be reduced by condensing the MEA removed in the gas phase back into the system.

4. CONCLUSIONS

In this work, five trihexyl-tetradecylphosphonium-based ionic liquids paired with superbasic anions, namely the, 1,2,4-triazolide, 1,2,3-triazolide, benzotriazolide, benzimidazolide, and imidazolide were mixed in equimolar amounts with MEA and the effect on the CO₂ capture was investigated. The results showed that, depending on the anion structure, the presence of MEA could either increase or decrease the CO₂ capture ability. Increases in CO₂ capacity were only observed for [P₆₆₆₁₄]-[123Triz] and [P₆₆₆₁₄][Bentriz] ILs, and in these cases the two components were observed to work synergistically leading to an enhanced CO₂ capacity due to the formation of a stable IL/MEA complex. In all the other systems examined ideal behavior was observed. Importantly, while the addition of the MEA cosolvent decreased the viscosity compared with the pure IL, a large increase was seen upon absorption of CO₂ which was much higher than that found using water as the cosolvent. After careful investigation of these systems it is apparent that water has more potential as a cosolvent compared with MEA for CO₂ absorption. This is due to the large increase in viscosity upon CO₂ absorption in the presence of MEA making it unsuitable for industrial use.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.5b00710. Supporting data are openly available on Queen's University Research Portal <http://pure.qub.ac.uk/portal/en/datasets>.

¹H NMR spectra for synthesized ILs are available in Figure S1. Name, source, initial, and final purity of compounds used during this work are listed in Table S1. Data of the relative volatility of the MEA in each of the investigated mixtures, the viscosity of (water + IL) mixtures and the CO₂ solubility in each of the investigated mixture as the function of time are tabulated in Tables S2–S4, respectively (PDF)

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Notes

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